Chapter 3. The Second Law

Phenomena

1. A gas expands and fills the available volume, but does not spontaneously contract into a smaller one.

2. A hot body cools to the same temperature as its surroundings, but a body does not spontaneously get hotter than its environment.

3. Heating diamonds yields graphite, but heating graphite does not give diamonds. *[Diamond by chemical vapor deposition]*

4. When a ball (the system of interest) bounces on a floor, the ball does not rise as high after each bounce because there are inelastic losses in the materials of the ball and floor (that is, the conversion of kinetic energy of the ball's overall motion into the energy of thermal motion).

Conclusions

The direction of change leads to **the greater dispersal of the total energy**.

The First Law of Thermodynamics = Always Valid

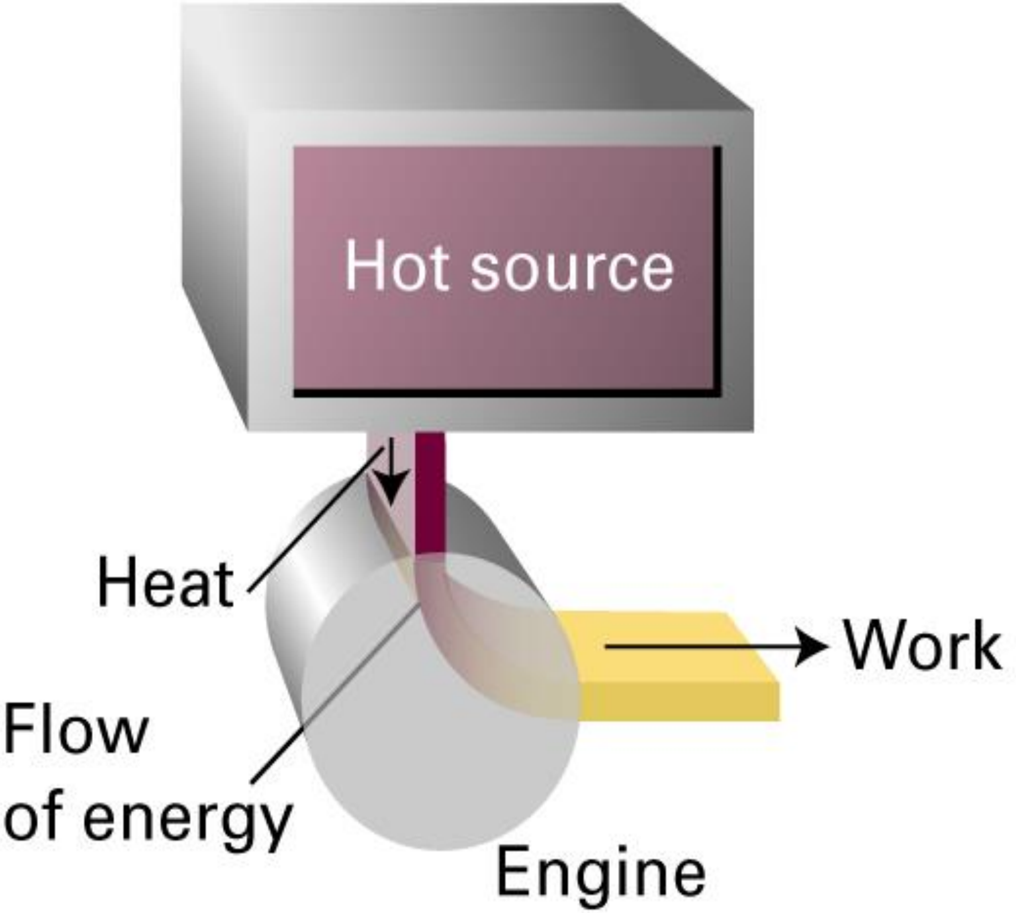


Figure 3A.3

The **Kelvin statement** of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change.

The process is not in conflict with the First Law because energy is conserved.

Irreversible
Video (*time or –time*)

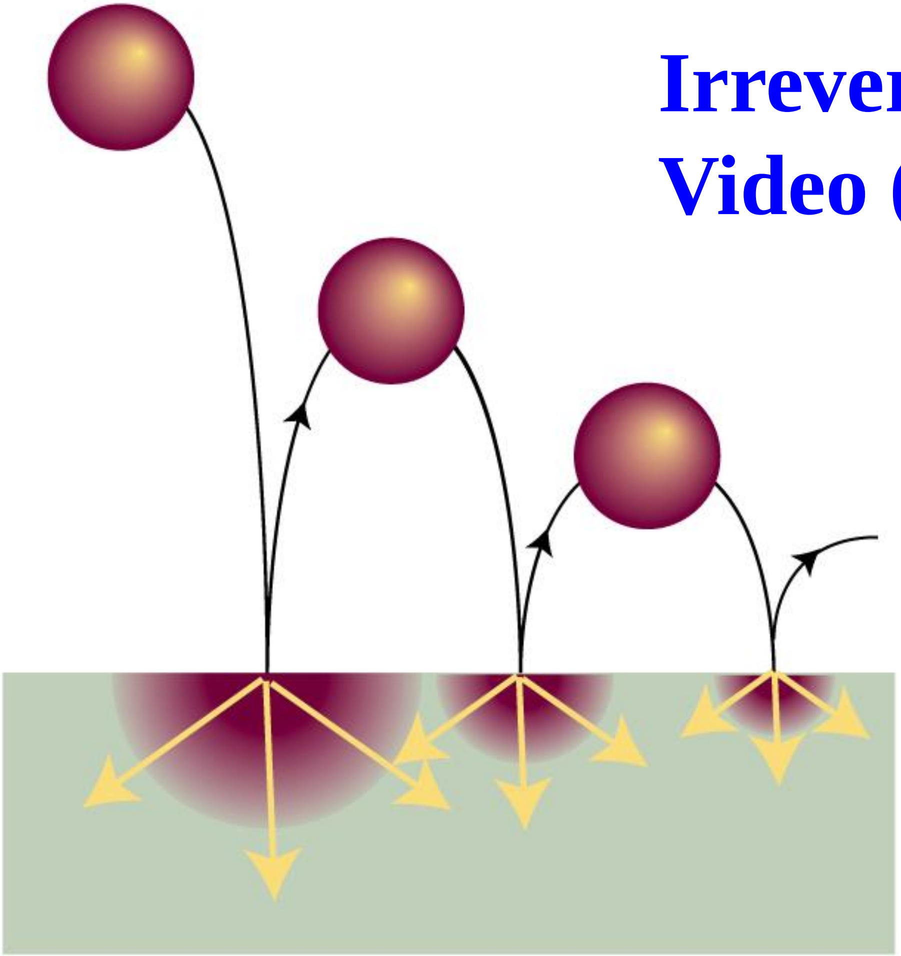


Figure 3A.1

The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a

macroscopic scale.

Random Motion

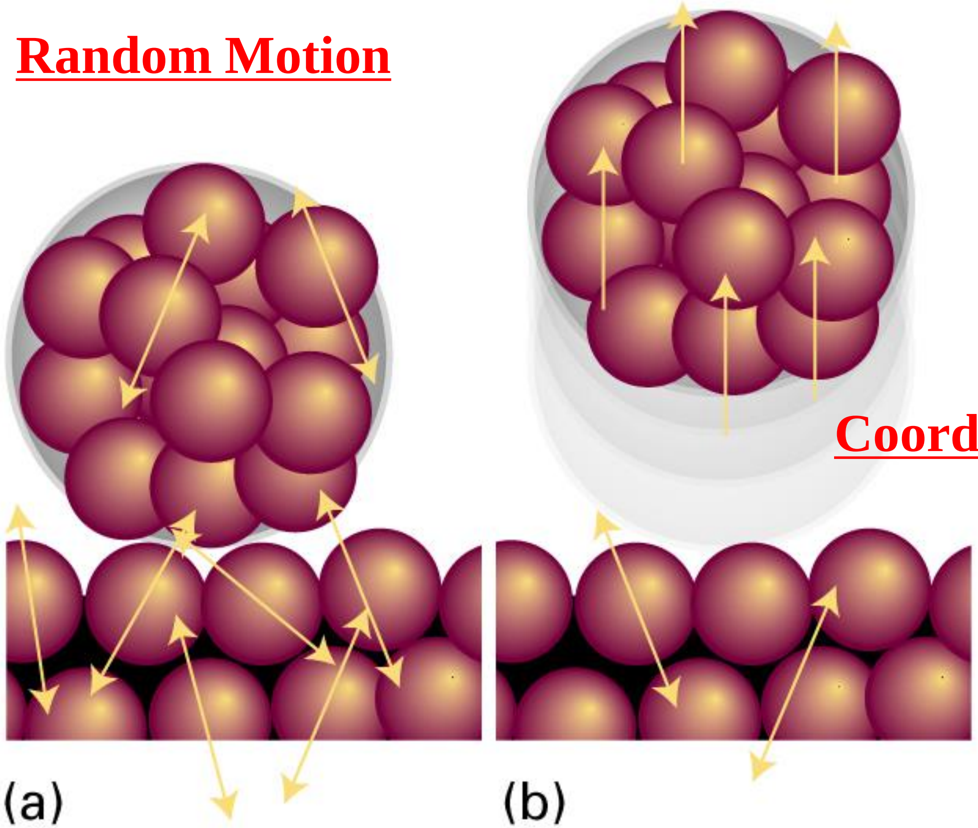


Figure 3A.2

Coordinated Motion

Macroscopic World

The molecular interpretation of the **irreversibility** expressed **by the Second Law**.

(a) A ball is resting on a warm surface, and the atoms are undergoing **thermal motion** (vibration, in this instance), as indicated by the arrows.

(b) For the ball to fly upwards, some of the random vibrational motion would have to change into coordinated, directed motion. Such a conversion is ***highly improbable***.

Measuring Dispersal: the Entropy of a System

Entropy *S*

1. A thermodynamic function that measures how the dispersal of energy alters when a system changes from one state to another.

2. **A state function**

- Statistical definition
- Thermodynamic definition

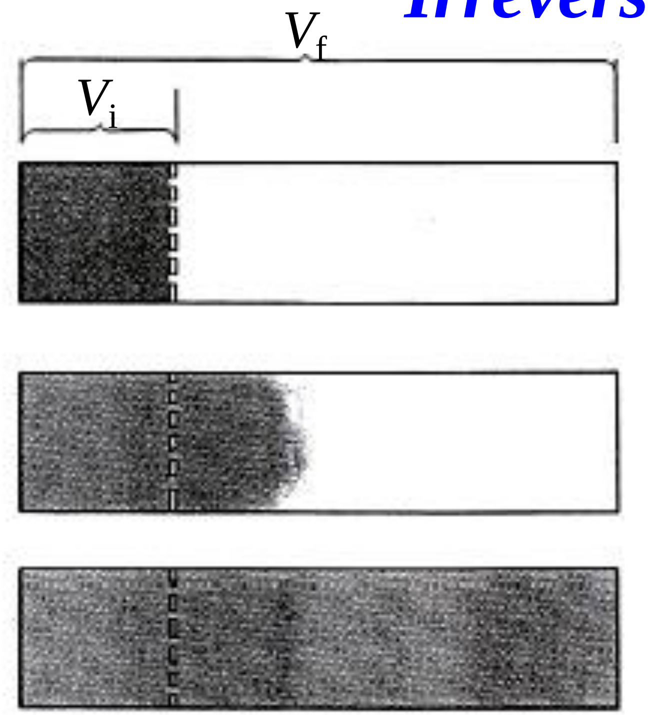
Statistical View of the Entropy

The direction of spontaneous change is:

- from a state with **low probability** of occurring

- to one of [redacted].

Irreversible



The direction of spontaneous change for a gas in a pair of connected vessels

Consider an Ideal Monatomic Gas:

Number of microstates of one atom being in V_i: $\omega(V_i) = cV_i$

Number of microstates that N atoms are in V_i: $\Omega(V_i) = [\omega(V_i)]^N = c^N V_i^N$

Number of microstates that N atoms are in V_f: $\Omega(V_f) = c^N V_f^N$

Entropy S ∝ (??) Number of Microstates Ω

[White Board]

$S = \Omega \rightarrow$ not **extensive**

$S(N, V, T) = k \ln \Omega(N, V, T)$ where k is some constant, Boltzmann constant.

When an ideal gas expands isothermally from V_i to V_f,

$$\Delta S = S(V_f) - S(V_i) = k \ln (cV_f)^N - k \ln (cV_i)^N$$

$$= kN(\ln cV_f - \ln cV_i) = kN \ln \frac{V_f}{V_i}$$

$N = nN_A$ where n: the number of moles, N_A: Avogadro's number

$$\Delta S = nR \ln \frac{V_f}{V_i}, \quad kN_A = R$$

Ideal Gas
Isothermal

(3A.14)

$$\Delta S = nR\ln\frac{V_f}{V_i} = Nk_B\ln\frac{V_f}{V_i}, \quad k_B N_A = R$$

Ideal Monoatomic Gas
Isothermal

Assumptions of this calculation

1) Ideal gas: neglect the interaction between particles and neglect rotational and vibrational modes.

2) Isothermal process: $\left(\frac{\partial U}{\partial V}\right)_T = 0$

Entropy measures the dispersal of energy, and the natural tendency of spontaneous change is towards the states of higher entropy.

$$S(N,V,T) = k_B \ln \Omega(N,V,T)$$

(3A.5)

Ω = Number of Microstates

위치, 방향, 진동, 전자 분포, 전자 춤, etc.

Same *E*

[White Board]

Thermodynamic View of Entropy

Thermal energy → random motion

1. A change in entropy dS is proportional to the amount of heat added dq. **[Extensive Properties]**

2. Impact of dq on the chaos is inversely proportional to T.

For a given dq, the change in entropy is large when the temperature is low, but small if the temperature is high.

$$dS = \frac{\text{đ}q_{rev}}{T} \tag{3A.1}$$

The ratio of a randomizing influence (dq_{rev})
to a measure of the amount of randomness
already present (at T)

Never Definition

If the changes are restricted to reversible transfer of heat, then the quantity dq_{rev}/T is found to be a state function.

Ideal Gas
Isothermal

For a reversible and isothermal expansion ($V_i \rightarrow V_f$) of an ideal gas,

$$dU = dq + dw = 0$$

$$dq = -dw$$

$$dq_{rev} = pdV = \frac{nRT}{V}dV$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \cancel{dT} + \cancel{\left(\frac{\partial U}{\partial V}\right)_T} dV$$

0: isothermal

0: ideal gas

On integration:

$$\Delta q_{rev} = nRT \ln \frac{V_f}{V_i}$$

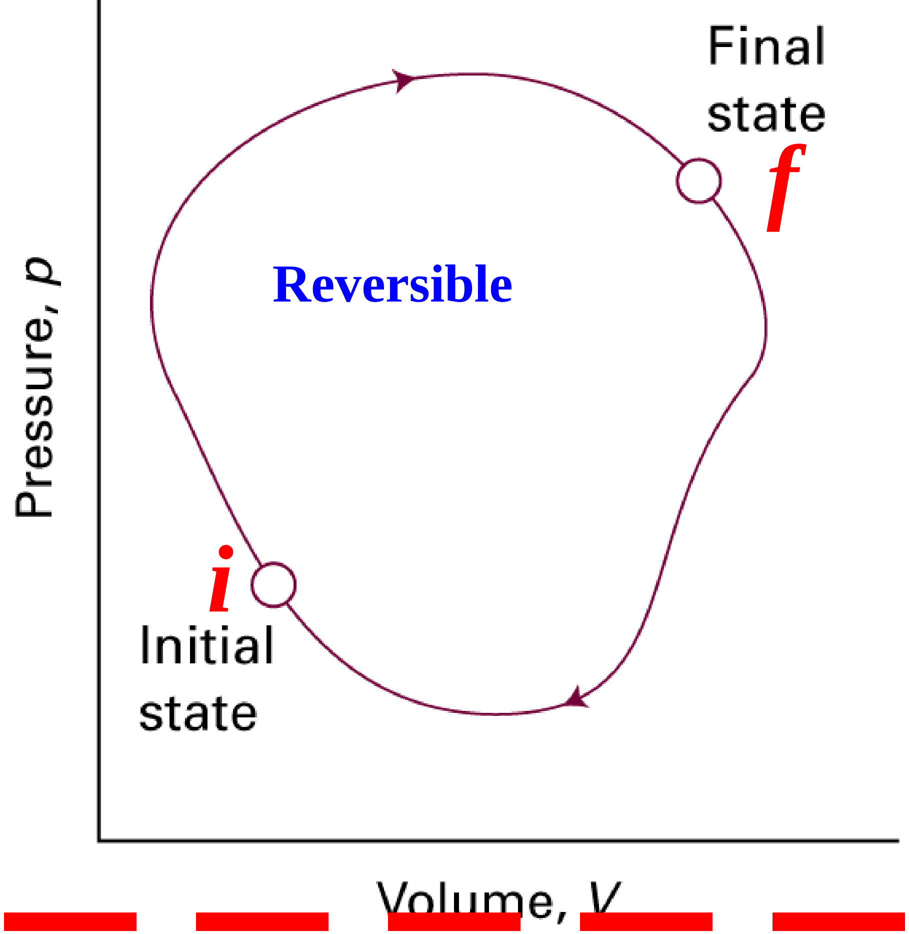
$$\Delta S = \int_i^f dS = \int_i^f \frac{dq_{rev}}{T} = \frac{1}{T}\int_i^f dq_{rev} = \frac{\Delta q_{rev}}{T}$$

열역학 2법칙 적용 (reversible 경우)

$$= \frac{nRT \ln(V_f / V_i)}{T} = nR \ln \frac{V_f}{V_i}$$

(same as pages 6 & 7)

Ideal Gas
Isothermal
(3A.14)



$$dS = \frac{\text{đ}q_{rev}}{T}$$

Figure 3A.6

In a thermodynamic cycle, the overall change in a **state function** (from the initial state to the final state and then back to the initial state again) is zero.

For an isolated system, no heat enters or leaves the system irreversively, i.e. $dq=0$.

This inequality shows that these spontaneous processes must lead to an increase in entropy of the universe.

The second law: In an **isolated system**, spontaneous processes occur ***in the direction of increasing entropy***.

$$\therefore \Delta S \geq 0$$

3A.4(b) Entropy Change Arising from a Phase Transition

Under the condition of constant pressure, the **latent heat** is an enthalpy of phase transition ΔH_t.

~0.5 eV/atom

***s*-Si ↔ *l*-Si**

그림 ***G*, *H*, & *S***

$$\Delta S = \frac{\Delta H_t}{T_t}$$

T_t : transition temperature

- ➢ Both melting and boiling are endothermic processes ($\Delta H_t > 0$). So, each is accompanied by an increase of the system's entropy.
- ➢ If the phase transition is exothermic ($\Delta H_t < 0$, as in freezing or condensing), then the entropy change is negative. This decrease in entropy is consistent with localization of matter and energy that accompanies the formation of a solid from a liquid or a liquid from a gas.
- ➢ If the transition is endothermic ($\Delta H_t > 0$, as in the melting and vaporization), then the entropy change is positive, which is consistent with dispersal of energy and matter in the system.

R = 8.314 J mol^{-1} K^{-1}

The entropy change of transition:

$$\Delta S(\text{methane}) = \frac{\Delta H_{evap,m}}{T_b} = \frac{9.27\times10^3}{111.8} = 83.1\, JK^{-1}mol^{-1}$$

$$\Delta S(\text{carbon tetrachloride}) = \frac{30\times10^3}{349.7} = 86\ JK^{-1}mol^{-1}$$

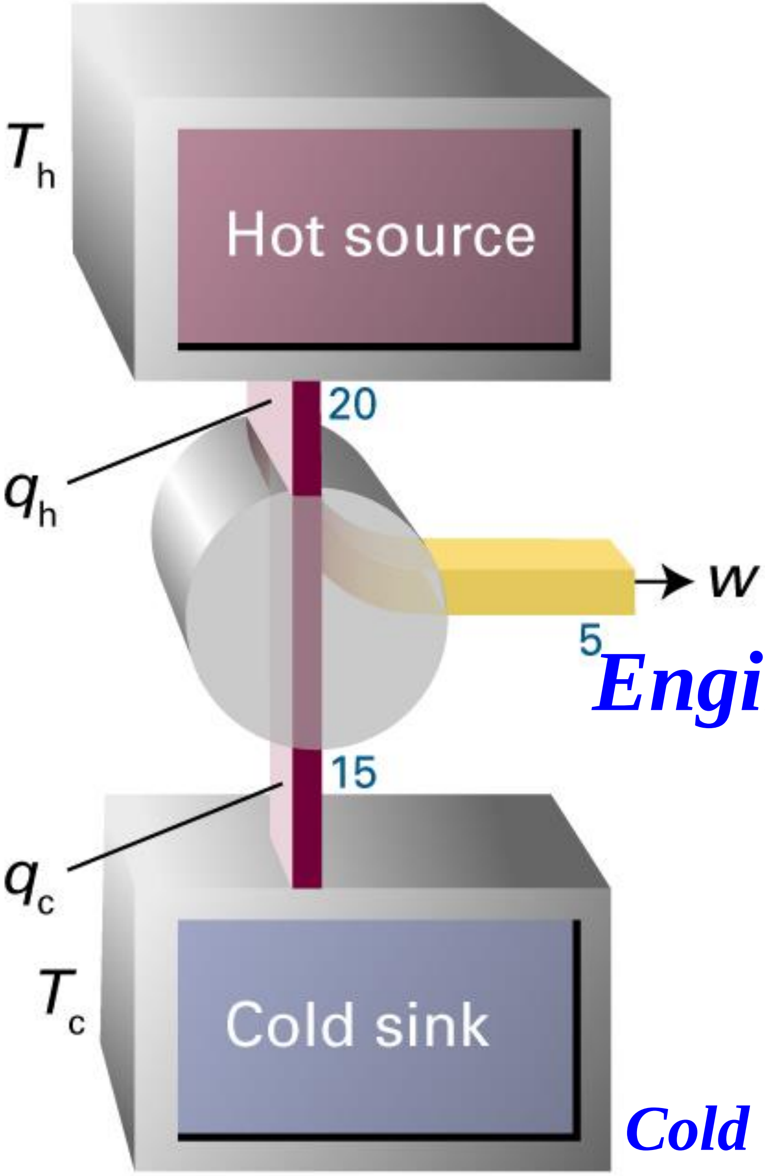
A wide range of liquids gives approximately the same entropy of vaporization. ⇒ Trouton’s rule **(page 122)**

$$\Delta S(\text{water}) = 109\ JK^{-1}mol^{-1}$$ large entropy change due to H-bonds

$$\Delta S \sim 10\, R/mol \ \sim 10\, k_B/molecule \qquad (\text{liquid} - \text{vapor})$$

$$\Delta S \sim \ 1\, R/mol \ \sim \ 1\, k_B/molecule \qquad (\text{solid} - \text{liquid})$$

Engine



Engine

Cold Reservoir

Figure 3A.8

Suppose:

An energy q_h (for example, 20 kJ) is supplied to the engine, and

q_c is lost from the engine (for example, $q_c = -15$ kJ), and **discarded into the cold reservoir**.

The work done by the engine is equal to $q_\mathrm{h} + q_c$ (for example, 20 kJ + (–15 kJ) = 5 kJ).

The **efficiency** is the work done divided by the heat supplied from the hot source. **= 25%**

3A.3(a) Reversible Heat Engine: The Efficiency

Since the temperature of a cold reservoir is lower than that of a hot one, an overall increase of entropy can be produced even if q_h is withdrawn from the hot reservoir, and less than q_h is transferred to the cold.

$$\Delta S_{total} = \frac{q_c}{T_c} - \frac{q_h}{T_h} = 0$$ is zero.

Reversible change by an infinitesimal modification

Therefore, we are free to use some kind of device, an engine, to draw off the difference $(q_h - q_c)$ as work.

The **work** that an engine may produce is:

$$w'_{\max} = q_h - q_c = q_h\left(1 - \frac{T_c}{T_h}\right)$$

Reversible Engine = Maximum Work

The Carnot efficiency (ε) is the ratio of the maximum work generated to the heat absorbed.

$$\varepsilon = \frac{w'_{\max}}{q_h} = 1 - \frac{T_c}{T_h} \qquad \text{(3A.9)}$$

Example:

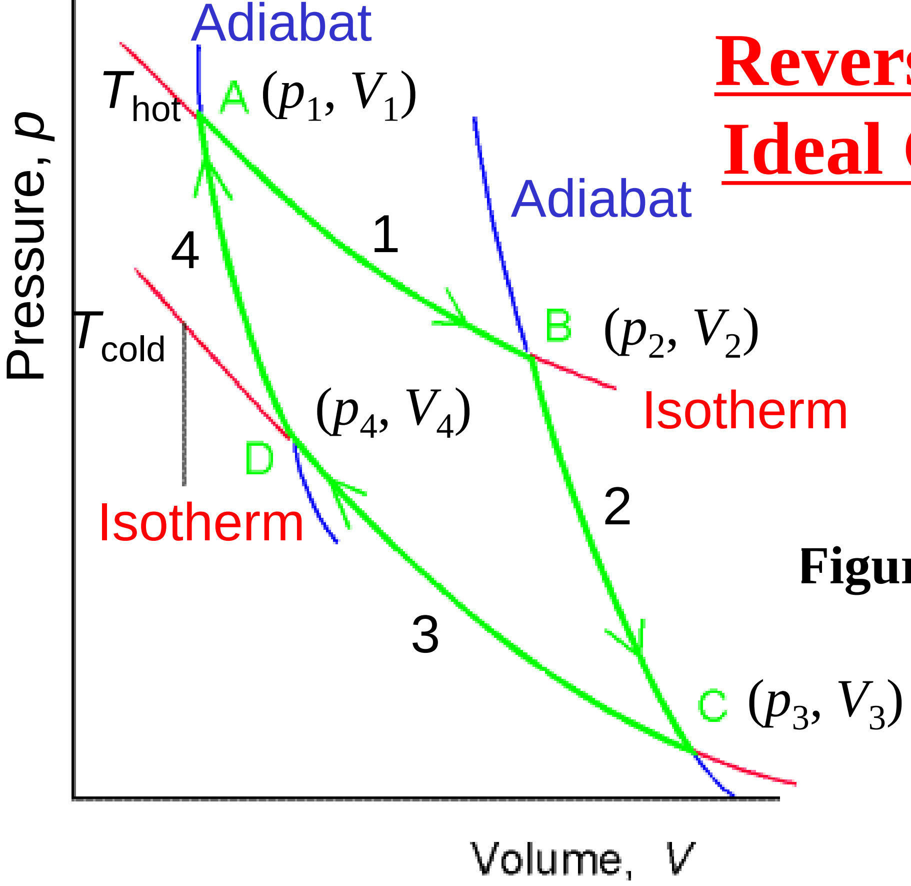
Calculate the Carnot efficiency (reversible heat engine) of an internal combustion engine where T_h = 3200 K and T_c = 1400 K.

Solution:

$$\varepsilon = 1 - \frac{1400}{3200} = 0.56 = 56\%$$

Compare with the practical efficiency ($\varepsilon \approx$ 25%) of internal combustion engines.

Basic Structure of a Carnot Cycle



Reversible Ideal Gas

Figure 3A.7

Step 1: Reversible isothermal expansion at temperature T_h.

Step 2: Reversible adiabatic expansion in which the temperature falls from T_h to T_c .

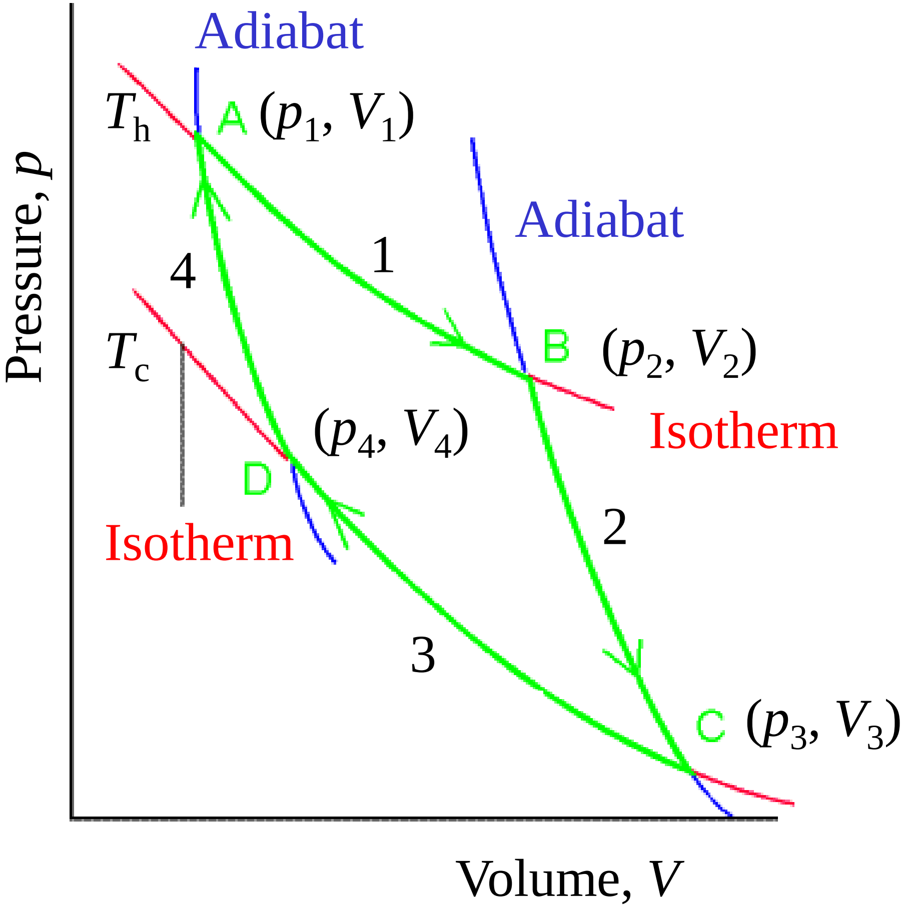
Step 3: Reversible isothermal compression at T_c.

Step 4: Reversible adiabatic reversible compression,

Restores the system to its initial state.

The Carnot Cycle

All engines work on a cycle.



Step 1 [Isothermal at q_h].

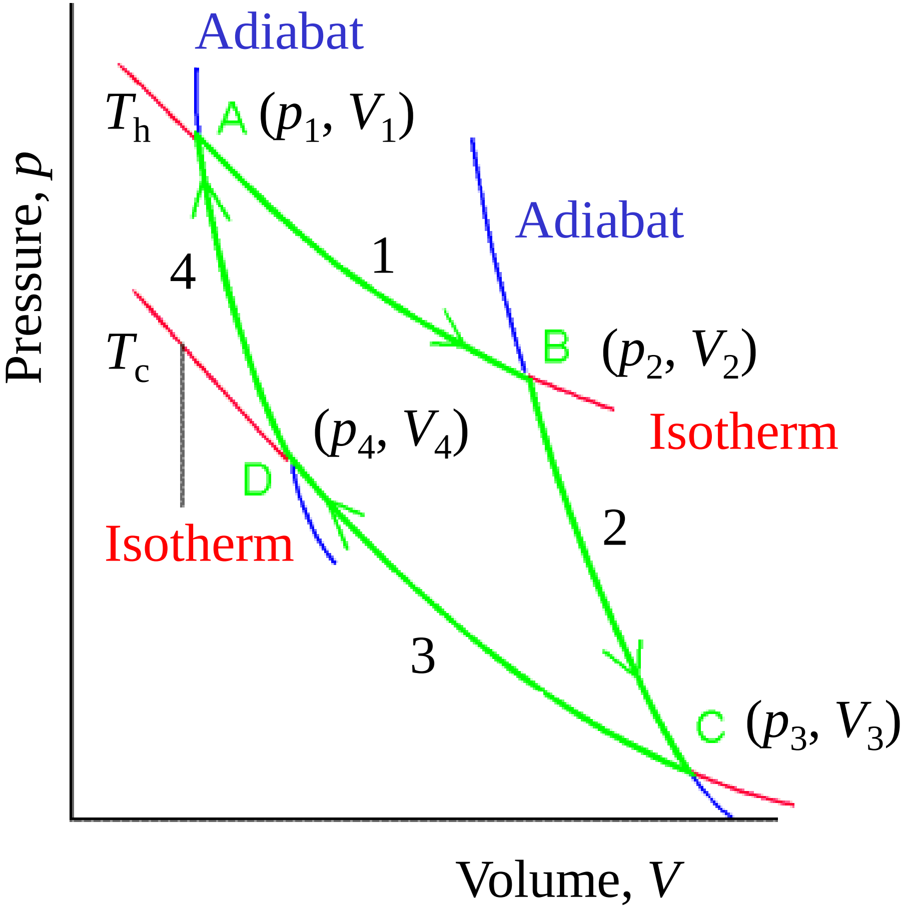
The gas absorbs heat (q_h) from the high-temperature resorvoir (temperature T_h) and expands isothermally and reversibly from V_1 to V_2.

$$q_h = RT_h \ln \frac{V_2}{V_1} \qquad \textbf{(3A.14)}$$

$$w = -RT_h \ln \frac{V_2}{V_1}$$

$$\Delta U = 0$$

(since isothermal, ideal gas)



Step 2 [Adibatic].

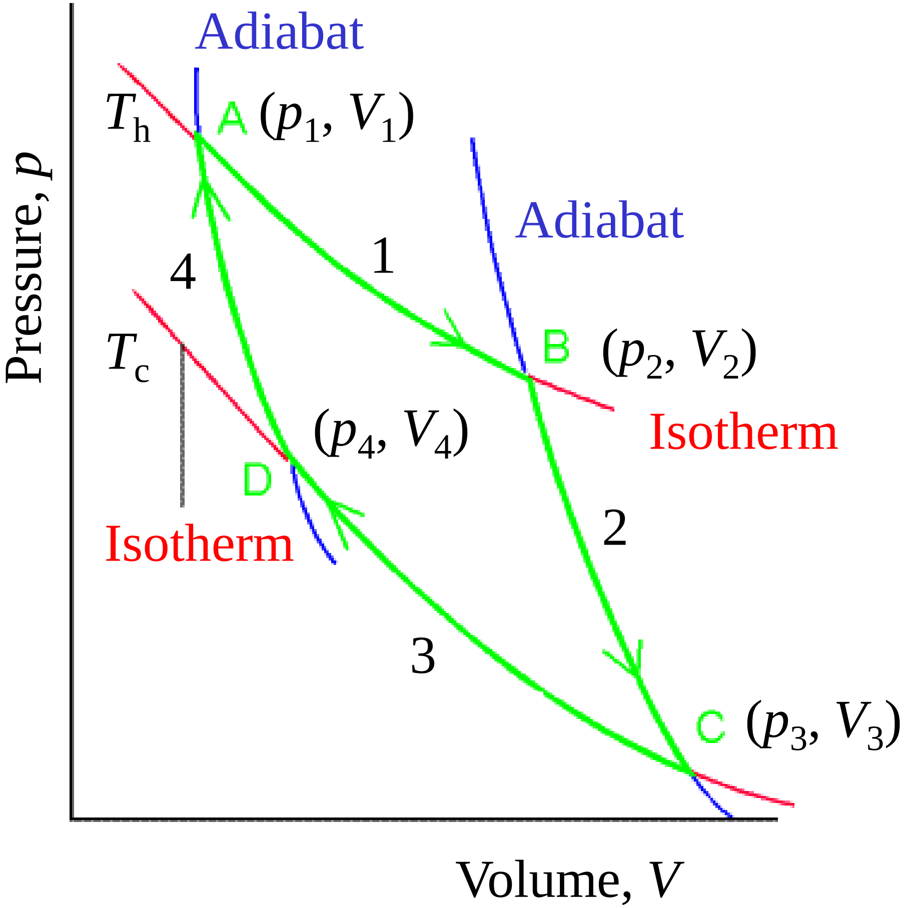
The gas expands adiabatically and reversibly from V_2 to V_3; in doing so, its temperature drops from T_h to T_c.

$$q = 0$$

$$w = \Delta U = \int_{T_h}^{T_c} C_V dT$$

Ideal gas

from $dU(V,T) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$



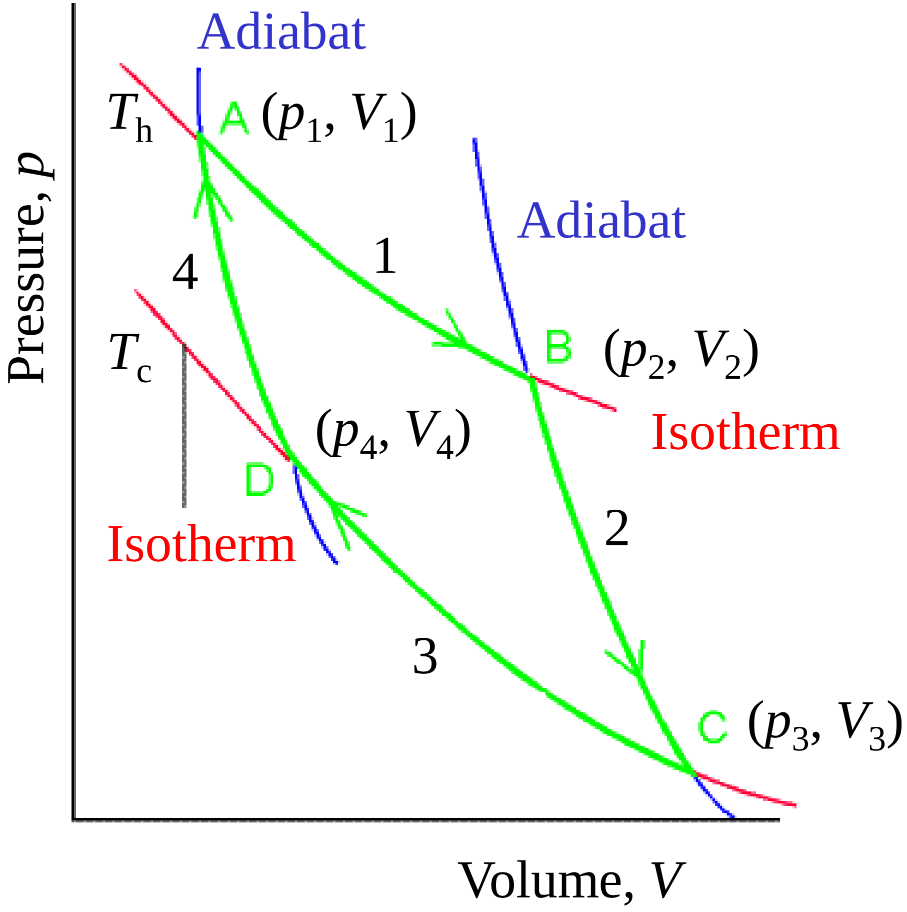
Step 3 [Isothermal at q_c].

The gas is compressed from V_3 to V_4 while in thermal contact with the low temperature resorvoir (temperature T_c), isothermally and reversibly.

$$q_c = RT_c \ln \frac{V_4}{V_3}$$

$$w = -RT_c \ln \frac{V_4}{V_3}$$

$$\Delta U = 0$$



Step 4 [Adibatic].

The gas is compressed adiabatically and reversibly from V_4 to V_1, warming in the process from T_c to T_h.

$$q = 0$$

$$w = \Delta U = \int_{T_c}^{T_h} C_V \, dT$$

Adding these together,

$$q(\text{cycle}) = q_h + q_c = \overset{\text{Step 1}}{RT_h \ln\frac{V_2}{V_1}} + \overset{\text{Step 3}}{RT_c \ln\frac{V_4}{V_3}}$$

$$w(\text{cycle}) = \overset{\text{Step 1}}{-RT_h \ln\frac{V_2}{V_1}} \underset{\text{Step 3}}{- RT_c \ln\frac{V_4}{V_3}}$$

$$\Delta U(\text{cycle}) = 0$$

For an ideal gas, and for reversible and adiabatic expansion*

$$C_{V,m} \ln\frac{T_f}{T_i} = -R \ln\frac{V_f}{V_i} \tag{2E.2b}$$

$$* dq = 0;\ dU = dw = -pdV \qquad dU = C_V dT.$$

$$c = \frac{C_V}{nR} = \frac{C_{V,m}}{R}$$

$$\ln\left(\frac{T_f}{T_i}\right)^c = \ln\left(\frac{V_i}{V_f}\right)$$

$$w(\text{cycle}) = -RT_h \ln\frac{V_2}{V_1} - RT_c \ln\frac{V_4}{V_3}$$

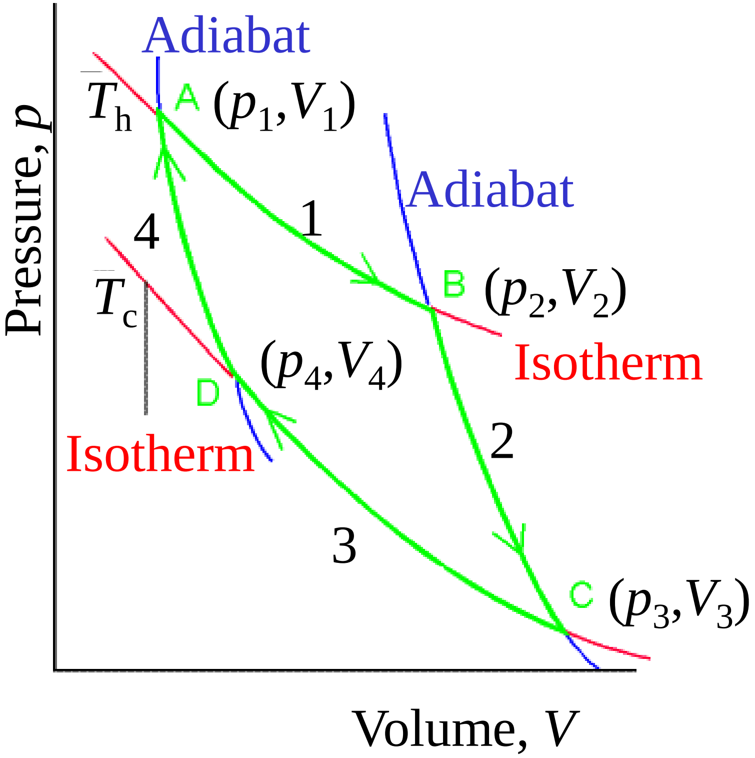
Apply the relation to the steps 2 and 4:

$$C_{V,m}\ln\frac{T_h}{T_c} = -R\ln\frac{V_2}{V_3} = -R\ln\frac{V_1}{V_4}$$

$$\therefore \frac{V_2}{V_3} = \frac{V_1}{V_4} \Rightarrow \frac{V_3}{V_4} = \frac{V_2}{V_1} \Rightarrow \ln\frac{V_2}{V_1} = -\ln\frac{V_4}{V_3}$$

$$\therefore -w = RT_h\ln\frac{V_2}{V_1} - RT_c\ln\frac{V_2}{V_1} = R(T_h - T_c)\ln\frac{V_2}{V_1}$$

$$q_h = RT_h\ln\frac{V_2}{V_1}$$



∴ The efficiency of a Carnot engine is the ratio of the net work (-*w*) to the **fuel burned to provide the heat q_h**.

$$\text{efficiency} = \frac{-w}{q_h} = \frac{T_h - T_c}{T_h} = 1 - \left(\frac{T_c}{T_h}\right)$$

(3A.10)

(same as page 14)

Any Reversible Cycle

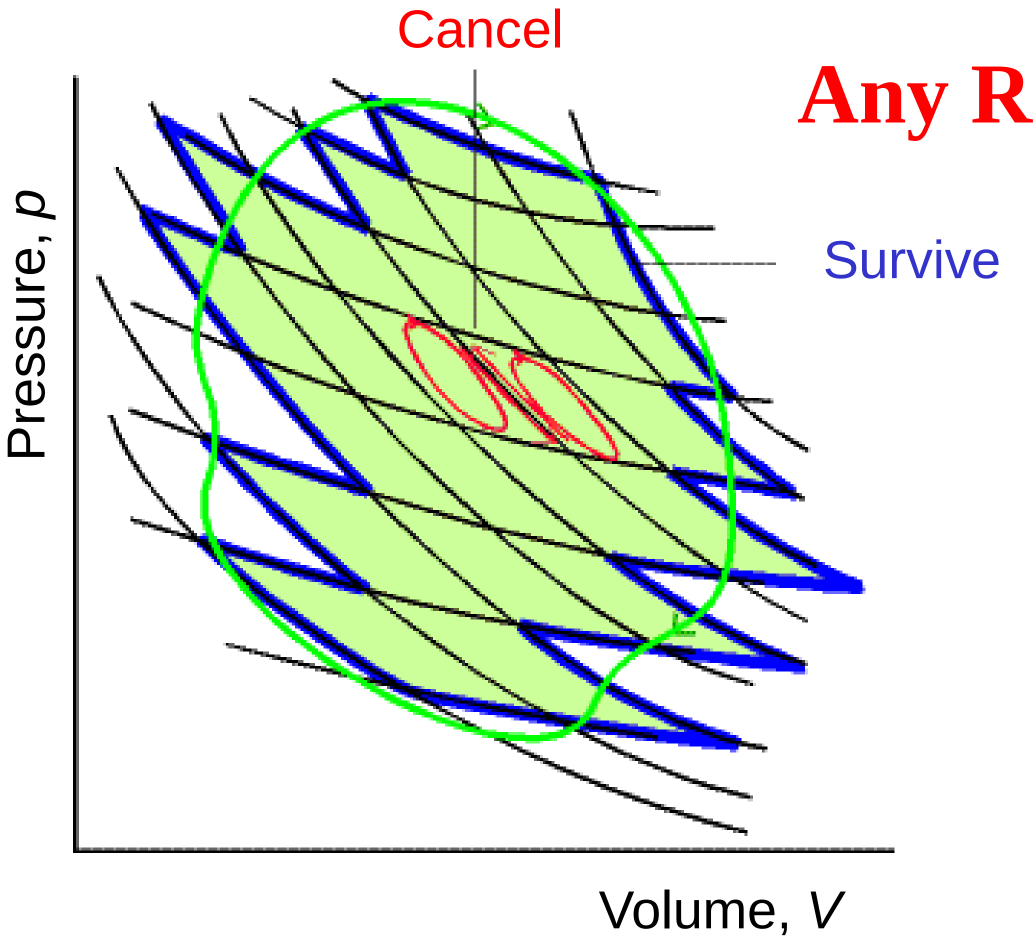


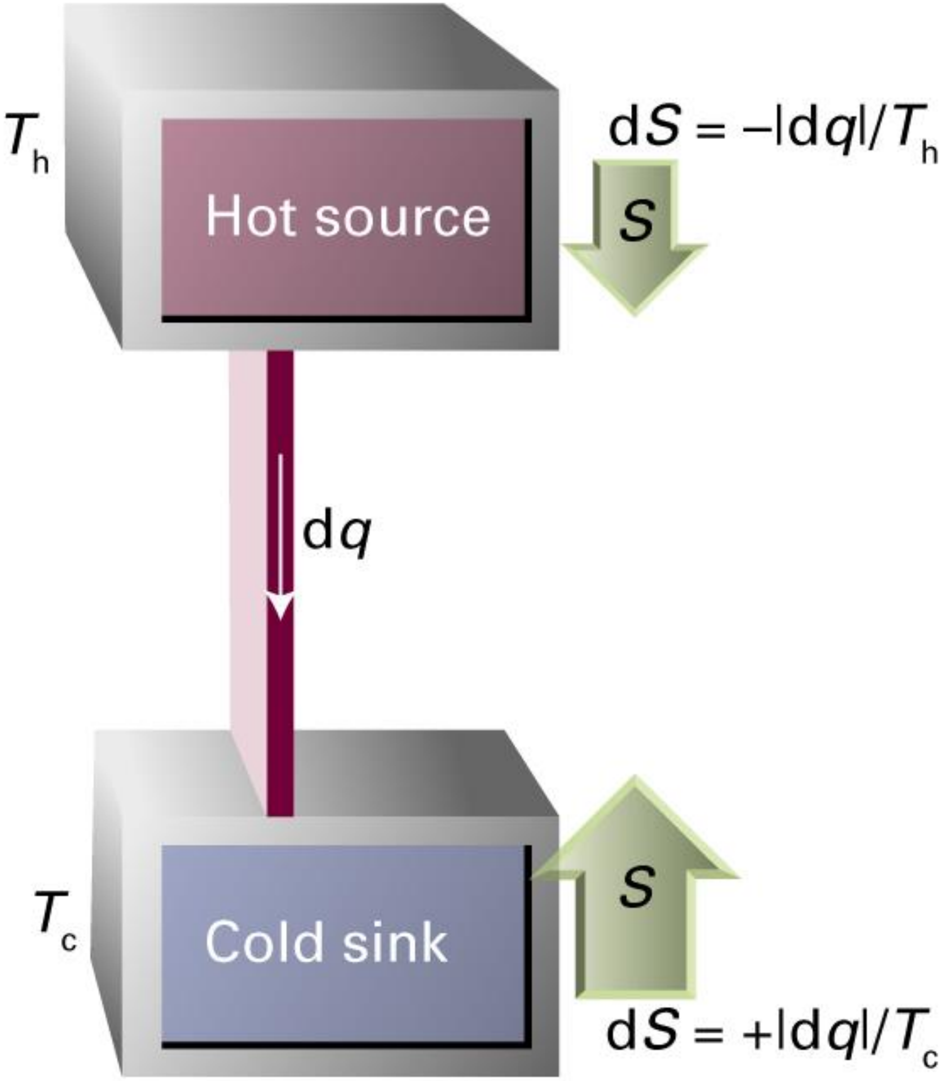
Figure 3A.10

A general cycle can be divided into small Carnot cycles. The match is exact in the limit of infinitesimally small cycles. Paths cancel in the interior of the collection, and **only the perimeter**, an increasingly good approximation to the true cycle as the number of cycles increases, survives.

Because the energy or entropy change around every individual cycle is zero, the integral of the **energy or entropy around the perimeter is zero** too.

(skip)

Brief Illus. 3A.6



When energy leaves a hot reservoir as heat, the entropy of the reservoir decreases.

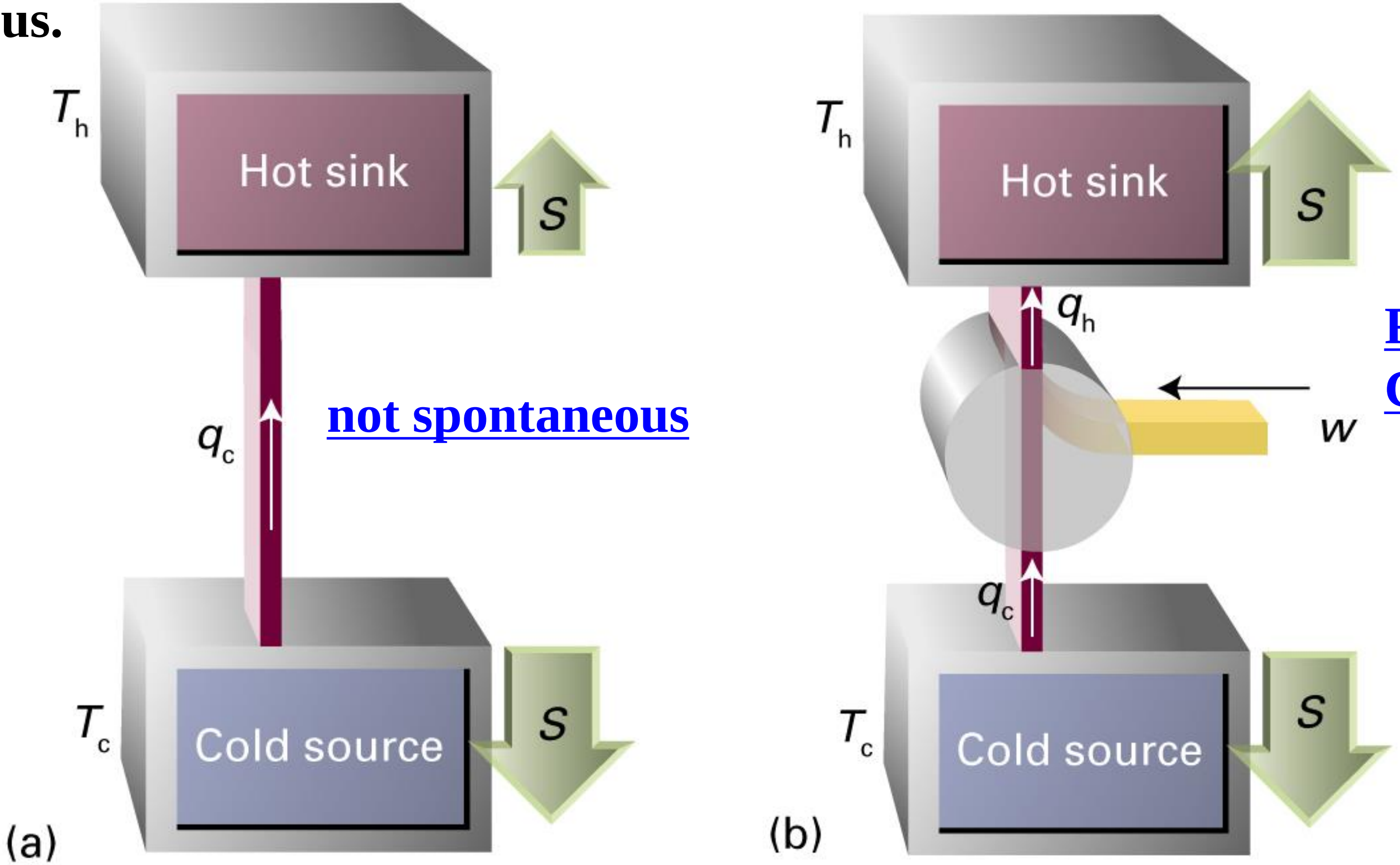
When the same quantity of energy enters a cooler reservoir, the entropy increases by a larger amount.

Hence, overall there is an increase in entropy and **the process is spontaneous.**

Relative changes in entropy are indicated by the sizes of the arrows.

Brief Illus. 3A.6

(skip)



not spontaneous

Reverse of Carnot Cycle

(a) The flow of energy as heat from a cold source to a hot sink is **not spontaneous**. As shown here, the entropy increase of the hot sink is smaller than the entropy decrease of the cold source, so there is a net decrease of entropy.

(b) The process becomes feasible if work is provided to add to the energy stream. Then the increase of entropy of the hot sink can be made to cancel the entropy decrease of the cold source.

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3C Concentrating on the System (p. 131)

The criterion for **natural, spontaneous change** solely in terms of the properties of the system is:

i) Constant volume: $(dq)_V = dU$

$$dS - \frac{dU}{T} \geq 0 \qquad TdS \geq dU$$ for spontaneous

ii) Constant pressure: $(dq)_p = dH$

$$dS - \frac{dH}{T} \geq 0 \qquad TdS \geq dH$$ for spontaneous

$$dS - \frac{dq}{T} \geq 0$$

Now one can **define** new thermodynamic functions for the criterion of spontaneous process.

i) Helmholz function: $A \equiv U - TS$

ii) Gibbs function: $G \equiv H - TS$

*****

At constant temperature, $dA = dU - TdS$ $\qquad$ $dG = dH - TdS$

Chap. 3C.1(c) (skip)

A: maximum work function or work function

Consider an isothermal system changing reversibly and delivering maximum work.

$$dU = dq_{rev} + dw_{rev}$$

$$dA = dU - TdS = dq_{rev} + dw_{rev} - TdS$$

Since $TdS = dq_{rev}$,

$$\therefore dA = dw_{rev}$$ at constant temperature

It follows that if we know ΔA for a process, we also know the maximum amount of work that the system can do. $\left(-w_{rev} = -\Delta A\right)$

(skip)

3C.1(e) Some Remarks on the Gibbs Function

$$\Delta G = G_{prod} - G_{react}$$

$$dH = dU + d(pV) = dq_{rev} + dw_{rev} + d(pV)$$

At constant temperature

$$dG = dH - \cancel{TdS} = dq_{rev} + dw_{rev} + Vdp + pdV - \cancel{TdS}$$

$$= dw_{rev} + Vdp + pdV$$

where dw_{rev} is the maximum work of the system (expansion work (-pdV) + other kinds of work).

$$dG = -\cancel{pdV} + dw_{e,\max} + \cancel{Vdp} + \cancel{pdV}$$

$$dG = dw_{e,\max}$$

0 (constant pressure)

At constant pressure and temperature, the change of the Gibbs function in a particular process gives the maximum extra work. This extra work is called the net work. $\left(-w_{e,\max} = -\Delta G\right)$

3B The Variation of Entropy with Temperature (constant *P*)

$$S(T_f) = S(T_i) + \int_i^f \frac{dq_{rev}}{T}, \qquad dq_{rev} = C_p dT$$

$$S(T_f) = S(T_i) + \int_i^f \frac{C_p dT}{T}$$

After Measuring C_p Experimentally, We Can Identify *S*(*T*), *H*(*T*) & *G*(*T*).

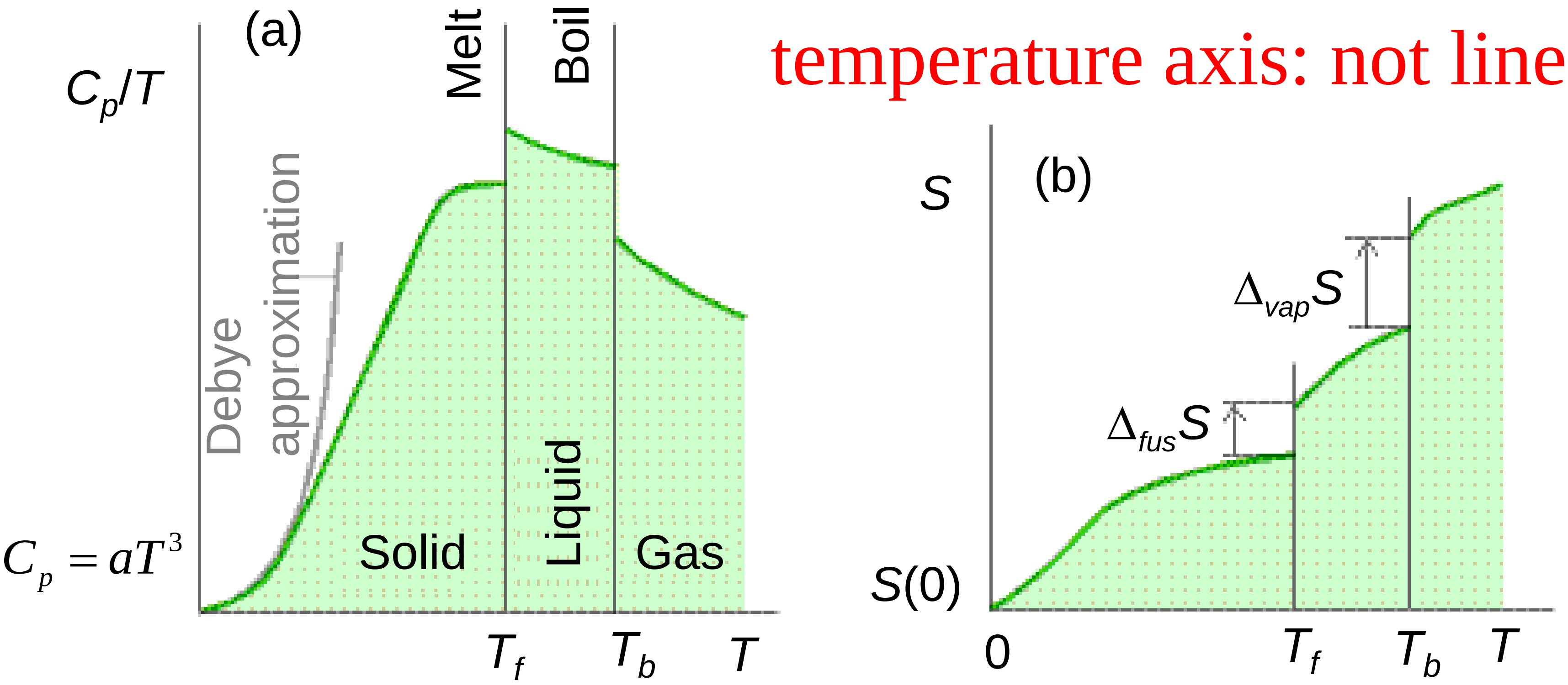
If C_p is independent of temperature in the temperature range of interest, we obtain

$$S(T_f) = S(T_i) + C_p \int_i^f \frac{dT}{T} = S(T_i) + C_p \ln\left(\frac{T_f}{T_i}\right)$$

At some temperatures between 0 and *T*, the materials may change its phase and absorb heat in the process.

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p^{solid}}{T} dT + \frac{\Delta H_{melt}}{T_f} + \int_{T_f}^{T_b} \frac{C_p^{liq}}{T} dT + \frac{\Delta H_{evap}}{T_b} + \int_{T_b}^{T} \frac{C_p^{gas}}{T} dT$$

In the vicinity of absolute zero: $C_p = aT^3$



temperature axis: not linear

Figure 3B.1

The determination of entropy from heat capacity data.

(a) The variation of C_p/T with the temperature for a sample.

(b) The entropy, which is equal to the area [in (a)] beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed.

Chapter 3B.2

At absolute zero, all quenchable energy has been quenched. In the case of a perfect crystal at absolute zero, all the atoms are in a regular, uniform array, and the absence of disorder and thermal chaos suggests that the entropy is the same in every case.

The Third Law of Thermodynamics:

All perfect crystals have the same entropy at absolute zero.

If the value zero is arbitrarily ascribed to the entropies of the elements (in the perfect crystalline form stable at $T = 0$ K),

then all perfect crystalline compounds also have zero entropies at absolute zero.

Chapter 3D Combining the First and Second Laws

$G = G(p, T, n)$ n: composition

Combining the first law and second law

The first law says

$$dU = dq + dw \qquad (1)$$

For **reversible** processes in the absence of any kind of work other than pV-work,

$$dw_{rev} = -pdV \qquad (2)$$

$$dq_{rev} = TdS \qquad (3)$$

$$dU = TdS - pdV \qquad (4)$$

→ Master equation or fundamental equation

$$dU = TdS - pdV$$

$$U = U(S,V)$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad (5)$$

Comparing eqs (4) and (5), we obtain relationships. $dU = TdS - pdV$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad (6)$$

$$-\left(\frac{\partial U}{\partial V}\right)_S = p \qquad (7)$$

Equation (6) enables a temperature to be expressed solely in terms of extensive thermodynamic quantities. If the volume is constant, the relation states that the ratio of the change in energy (a First Law concept) to the corresponding change in entropy (a Second Law concept) is equal to the temperature of the system, whatever its nature or composition.

3.8(a) Various Maxwell Relationships

$$dU = TdS - pdV \qquad (4)$$

U : exact differential

By using the relation No. 4,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad (8)$$

Maxwell relation

$$G = H - TS$$

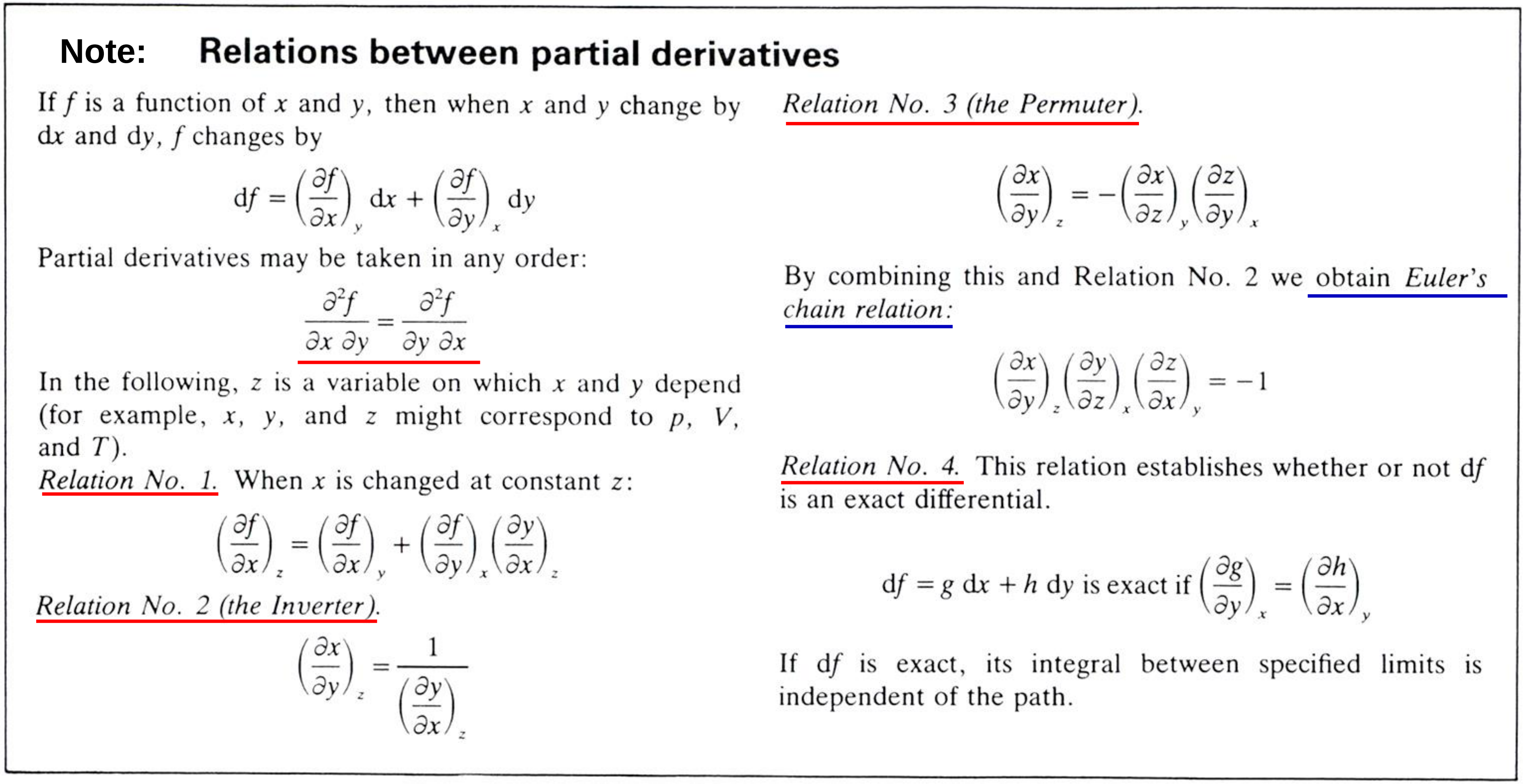
$$dG = \cancel{dU} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT \qquad \because dU = TdS - pdV$$

$$\because dG = Vdp - SdT \qquad (9)$$

G : exact differential

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \qquad (10)$$

Maxwell relation



Note: Relations between partial derivatives

If f is a function of x and y, then when x and y change by $\mathrm{d}x$ and $\mathrm{d}y$, f changes by

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y$$

Partial derivatives may be taken in any order:

$$\frac{\partial^2 f}{\partial x\,\partial y} = \frac{\partial^2 f}{\partial y\,\partial x}$$

In the following, z is a variable on which x and y depend (for example, x, y, and z might correspond to p, V, and T).

Relation No. 1. When x is changed at constant z:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

Relation No. 2 (the Inverter).

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\dfrac{\partial y}{\partial x}\right)_z}$$

Relation No. 3 (the Permuter).

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

By combining this and Relation No. 2 we obtain *Euler's chain relation:*

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Relation No. 4. This relation establishes whether or not $\mathrm{d}f$ is an exact differential.

$$\mathrm{d}f = g\,\mathrm{d}x + h\,\mathrm{d}y \text{ is exact if } \left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

If $\mathrm{d}f$ is exact, its integral between specified limits is independent of the path.

$$A = U - TS$$

$$dA = dU - TdS - SdT \qquad (11)$$

From equations (4) and (11)

$$dA = -pdV - SdT$$

A: exact differential

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad (12)$$

Maxwell relation

Maxwell relation

$$\begin{aligned} H &= U + PV \\ dH &= dU + pdV + Vdp \end{aligned} \tag{13}$$

From equations (4) and (13), $dU = TdS\text{-}pdV$

$$dH = TdV + Vdp$$

H : exact differential

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{14}$$

Maxwell relation

Maxwell relation

3D.1(b) The Variation of Internal Energy with Volume

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

(Sec. 2D.2)

Derivation

$$dU(S,V) = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad (5)$$

Dividing equation (5) by dV and imposing constant temperature,

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S \qquad (15)$$

Combining equations (6), (7) and (15), one can obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \qquad (16)$$

Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Substitution of equation (12) into equation (16)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad \textbf{(3D.6)}$$

Definition of internal pressure

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Example 3D.2

Show thermodynamically that $\left(\frac{\partial U}{\partial V}\right)_T$ is zero for an ideal gas, and compute its value for a van der Waals gas.

Solution:

For an ideal gas, $pV=nRT$.

$$\left(\frac{\partial p}{\partial T}\right)_T = \frac{nR}{V} \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

Combining two equations,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - p = 0$$

The equation of state of a van der Waals gas $p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb}$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V-nb} - p = \cancel{\frac{nRT}{V-nb}} - \left(\cancel{\frac{nRT}{V-nb}} - \frac{n^2a}{V^2}\right) = \frac{n^2a}{V^2}$$

ppt 2-61

3D. 2 Properties of the Gibbs Free Energy

$$G = H - TS$$

$$H = U + pV$$

$$dG = dH - TdS - SdT$$

$$= dU + pdV + Vdp - TdS - SdT \qquad (17)$$

Combining equation (4) and (17),

$$\therefore dG = TdS - pdV + pdV + Vdp - TdS - SdT$$

$$= Vdp - SdT \qquad (18)$$

$$G = G(p,T)$$

Master equation

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \qquad (19)$$

Combining eqs (18) and (19), one obtains

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S \qquad (20)$$

(3d.8)

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

(Chap. 5)

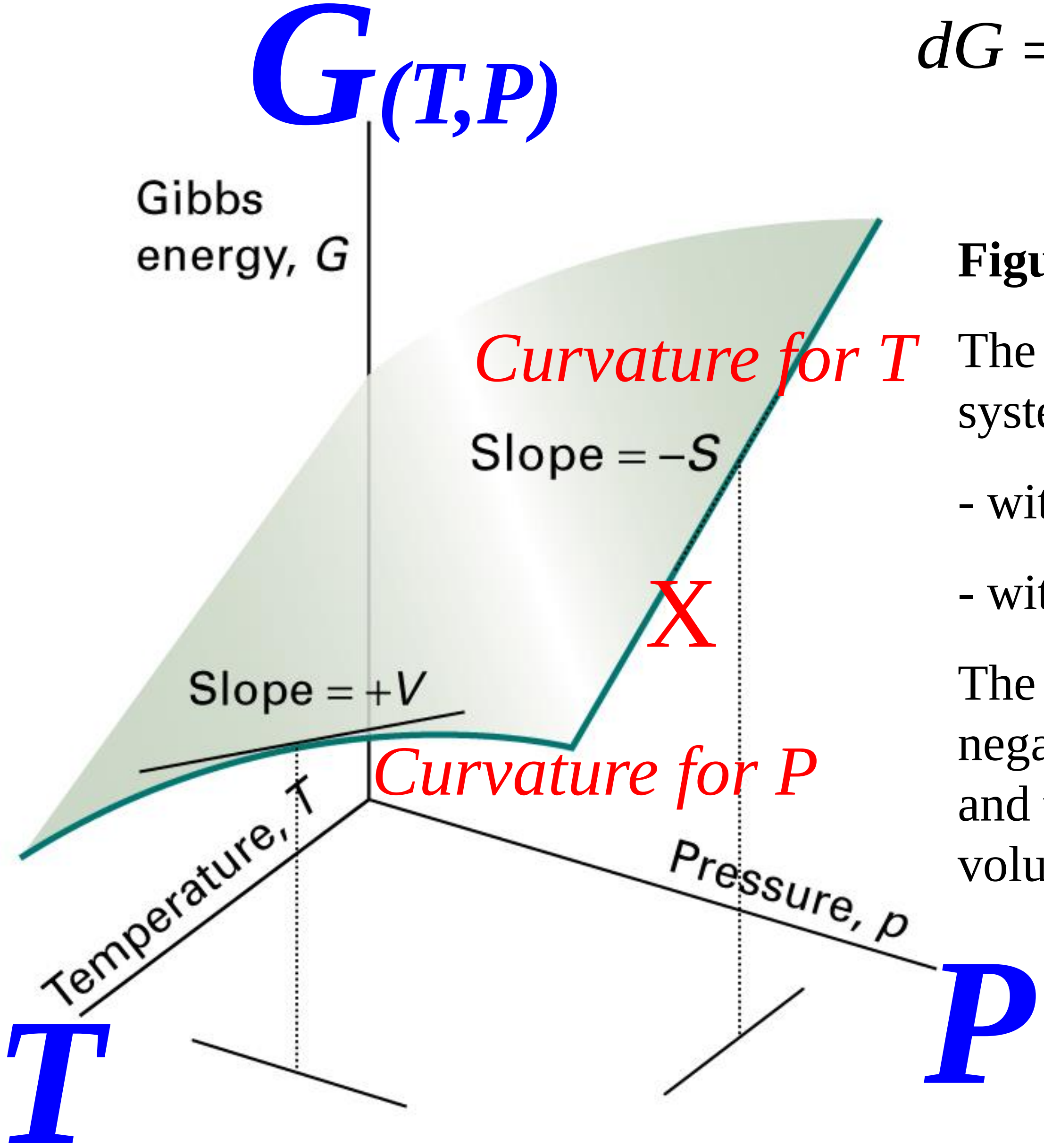


Figure 3D.1

The variation of the Gibbs energy of a system:

- with temperature at constant *P*

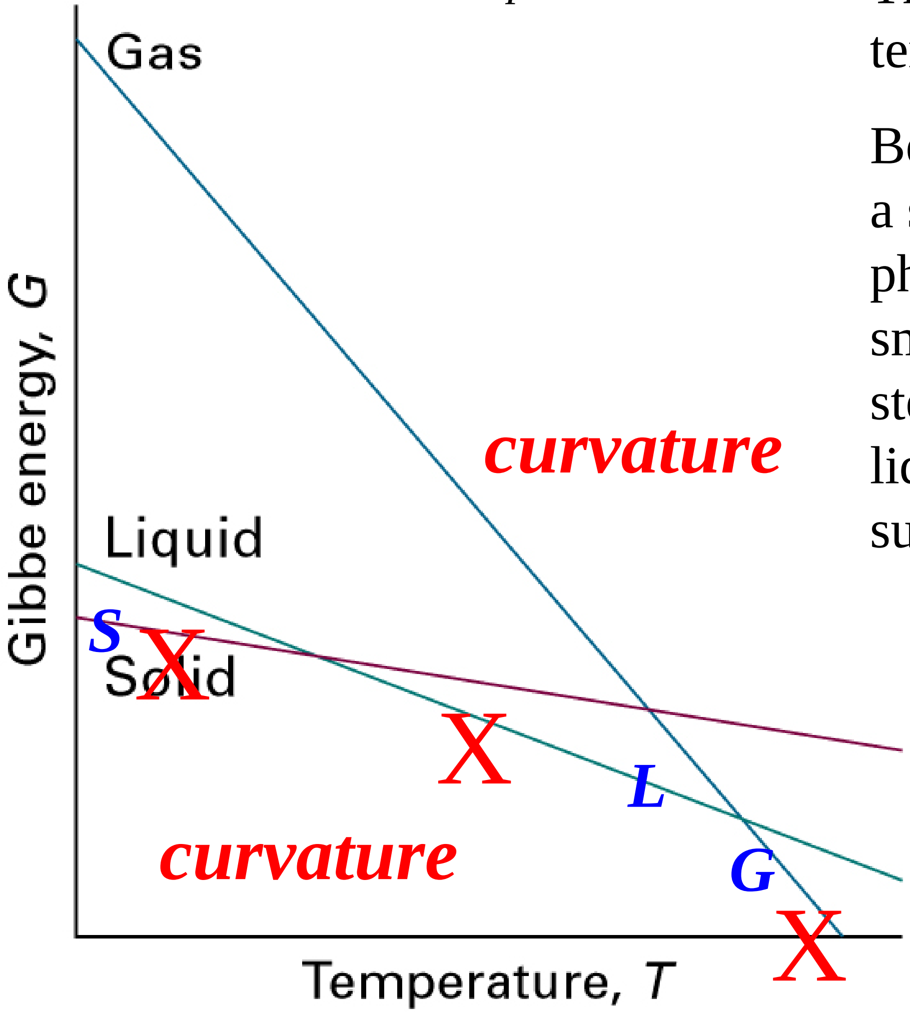
- with pressure at constant *T*

The slope of the former is equal to the negative of the entropy of the system and that of the latter is equal to the volume

Figure 3D.2

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$



The variation of Gibbs energy with the temperature is determined by the entropy.

Because the entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is smallest, the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.

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3D.2(b) The Change of Gibbs Energy with Temperature

Equation (20) implies that, as S is always a positive quantity, G must decrease when the temperature is raised at constant pressure (see Figure 3D.1).

$$G = H - TS \qquad S = \frac{H-G}{T} \qquad (21)$$

Combining eqs (20) and (21),

$$\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T} \qquad (22) \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\begin{aligned}\left(\frac{\partial (G/T)}{\partial T}\right)_p &= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\left(\frac{\partial}{\partial T}\left(\frac{1}{T}\right)\right)_p \\ &= \frac{1}{T}\left\{\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right\}\end{aligned} \qquad (23)$$

Combining eqs (22) and (23), one obtains

$$\underline{\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2}} \qquad (24) \qquad \boldsymbol{G(T) \to H(T)}$$

(3D.10)

Gibbs-Helmholtz equation

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$

For a chemical reaction,

initial state (**reactants**)→final state (**products**)

$$\Delta G = G_f - G_i$$

$$\left(\frac{\partial(\Delta G/T)}{T}\right)_p = -\left(\frac{H_f}{T^2} - \frac{H_i}{T^2}\right)$$

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_p = -\frac{\Delta H}{T^2} \qquad (25) \qquad \textbf{(3D.11)}$$

3D.2(c) The Change of Gibbs Free Energy with Pressure

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

For a reaction in which G_i changes to G_f,

$$\left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V, \quad \text{where } \Delta V = V_f - V_i.$$

Integration of the above equation results in

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V(p)\,dp \qquad (*) \qquad \textbf{(3D.12b)}$$

G is virtually independent of pressure for solid or liquid.

For **liquid or solid**, volume depends only very weakly on the pressure:

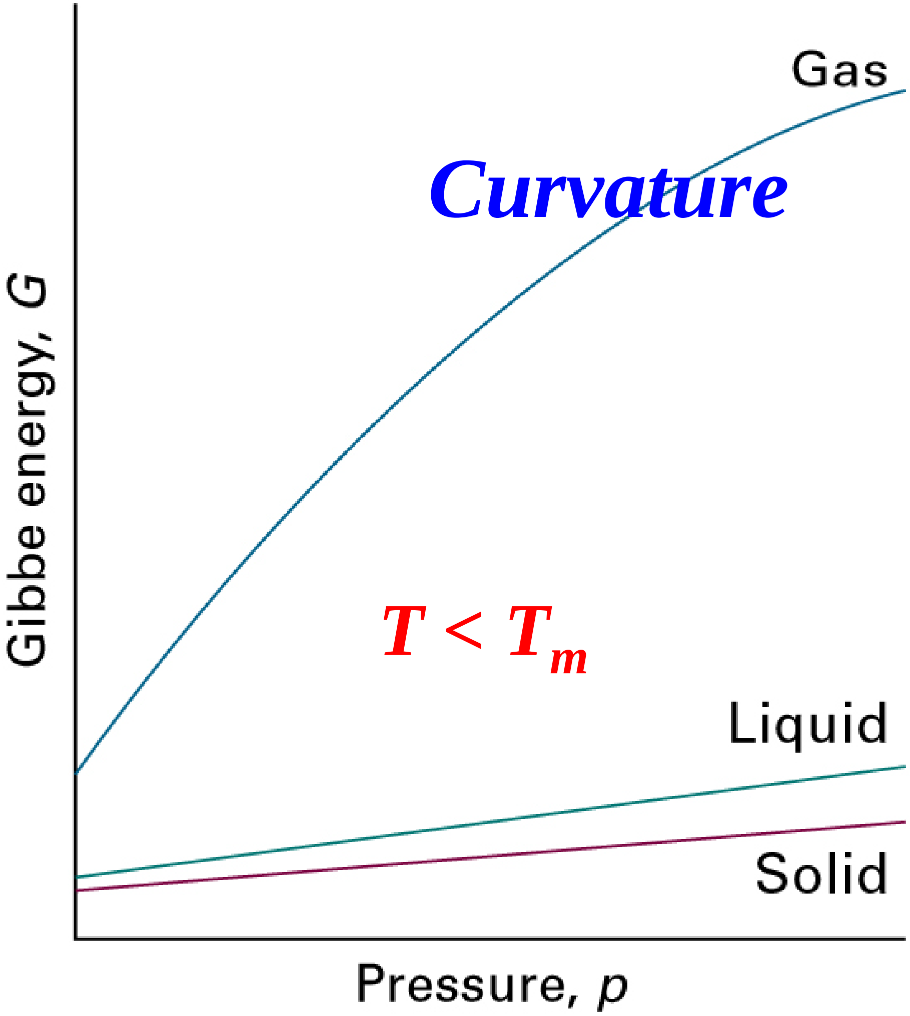
$$G_m(p_f) \cong G_m(p_i) + (p_f - p_i)V_m \qquad (\neq \text{지구과학})$$

Except at very high pressure, $(p_f - p_i)V_m$ is **very small** and virtually no error is introduced.

$\therefore$ For solids and liquids, $G_m(p_f) \approx G_m(p_i)$.

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

Figure 3D.3



Curvature

$T < T_m$

The variation of the Gibbs energy with the pressure is determined by the volume of the sample.

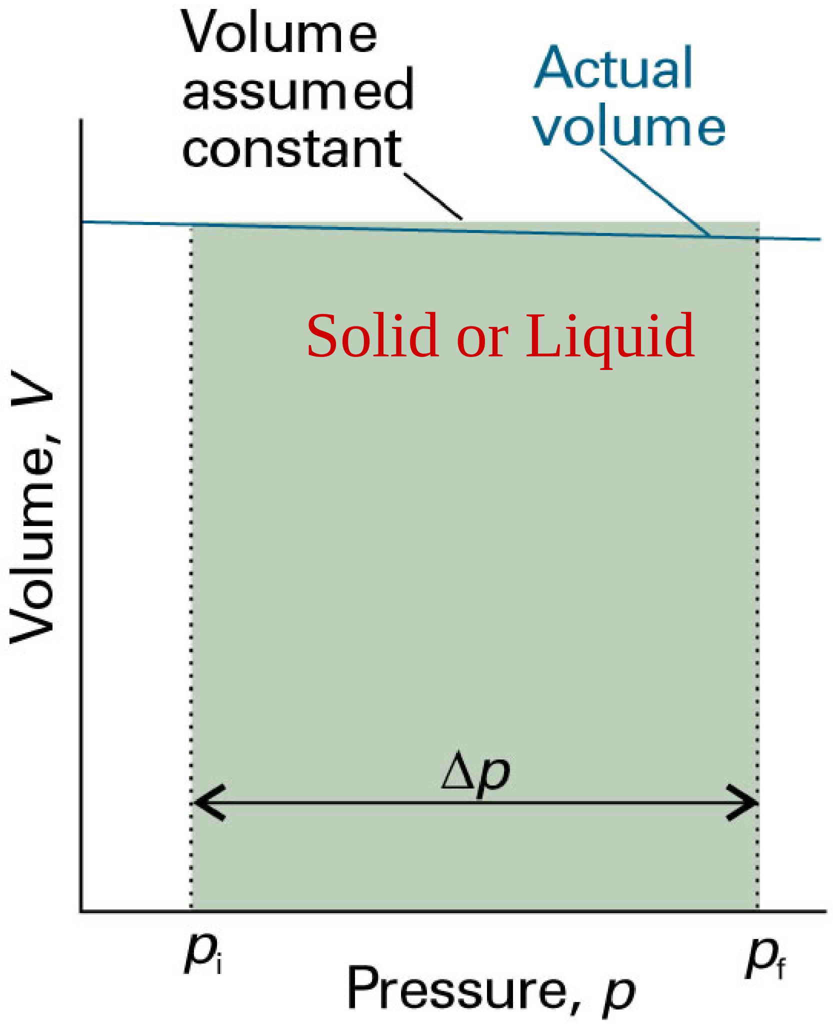
Because the volume of the gaseous phase of a substance is greater than that of the same amount of liquid phase, and the volume of the solid phase is smallest (for most substances), the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.

Because the volumes of the solid and liquid phases of a substance are similar, they vary by similar amounts as the pressure is changed.

$\sim 5\times10^{22}$ atoms / cm^3

for typical solid or liquid

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$ **(Chap. 5)**



$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V(p)dp$$

$$G_m(p_f) \cong G_m(p_i) + (p_f - p_i)V_m$$

$$\therefore \Delta G_m = V_m \Delta p$$

Figure 3D.4

The difference in Gibbs energy of a **solid or liquid** at two pressures is equal to the rectangular area shown.

We have assumed that the variation of volume with pressure is negligible.

Ideal Gas + Constant *T*

For an ideal gas, $V = \frac{nRT}{p}$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V(p)dp \qquad (*)$$

(3D.12b)

Inserting the above equation into equation (*) yields

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} \frac{nRT}{p} dp$$

$$\therefore G(p_f) = G(p_i) + nRT \ln \frac{p_f}{p_i}$$

Ideal Gas
constant *T*

(3D.15)

Ideal Gas constant *T*

$$G(p_f) = G(p_i) + nRT\ln\frac{p_f}{p_i}$$

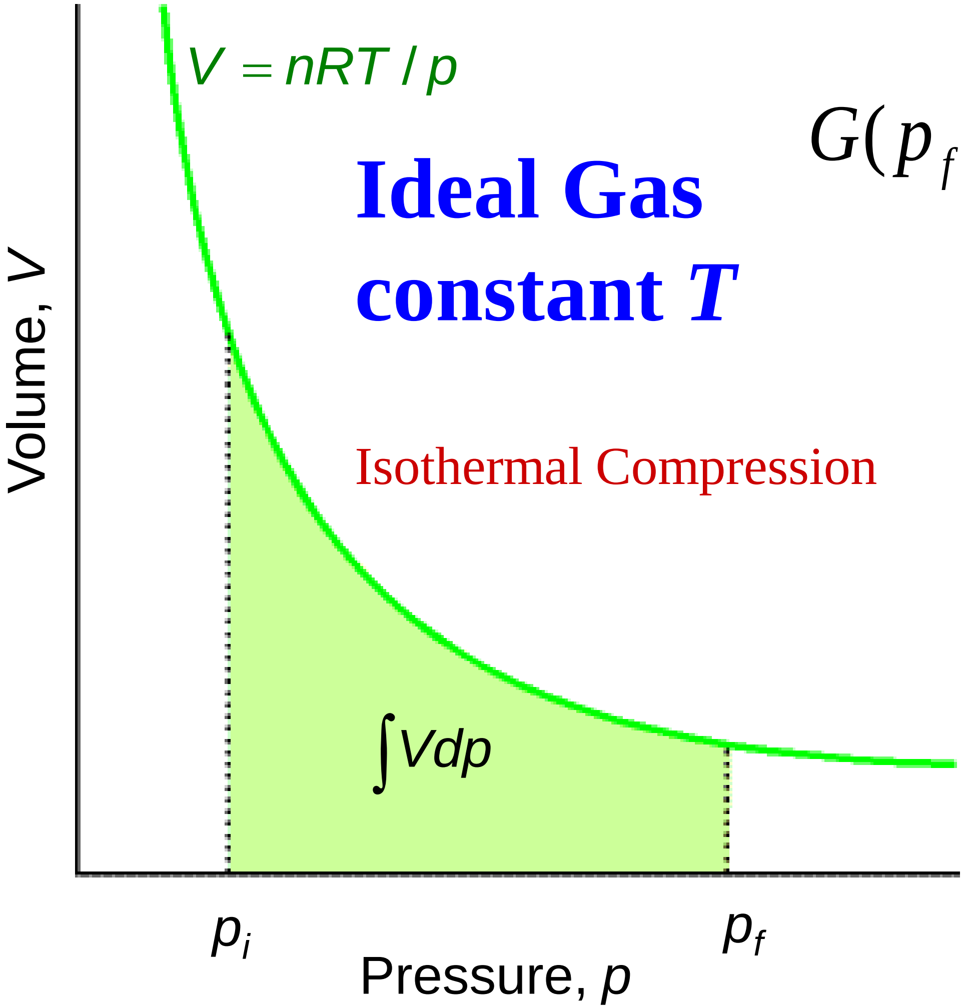


Figure 3D.5

The difference in Gibbs energy for a perfect gas at two pressures is equal to the area shown below the perfect-gas isotherm.

3D.2(c) Chemical Potential of an Ideal Gas

Standard state of an ideal gas = 1 *atm*

$$G(p_f) = G(p_i) + nRT\ln\frac{p_f}{p_i}$$

Gibbs function at 1 *atm* = G^0

At any other pressure *p*,

$$G(p) = G^0 + nRT\ln(p/atm)$$

For one mole of material,

$$G_m(p) = G_m^0 + RT\ln(p/atm)$$

Molar Gibbs Free Energy

We write $\mu = G_m(p)$:

Chemical Potential

$$\mu(p,T) = \mu^0(T) + RT\ln p$$

Ideal Gas **(3D.15)**

For a single component, chemical potential = G_m

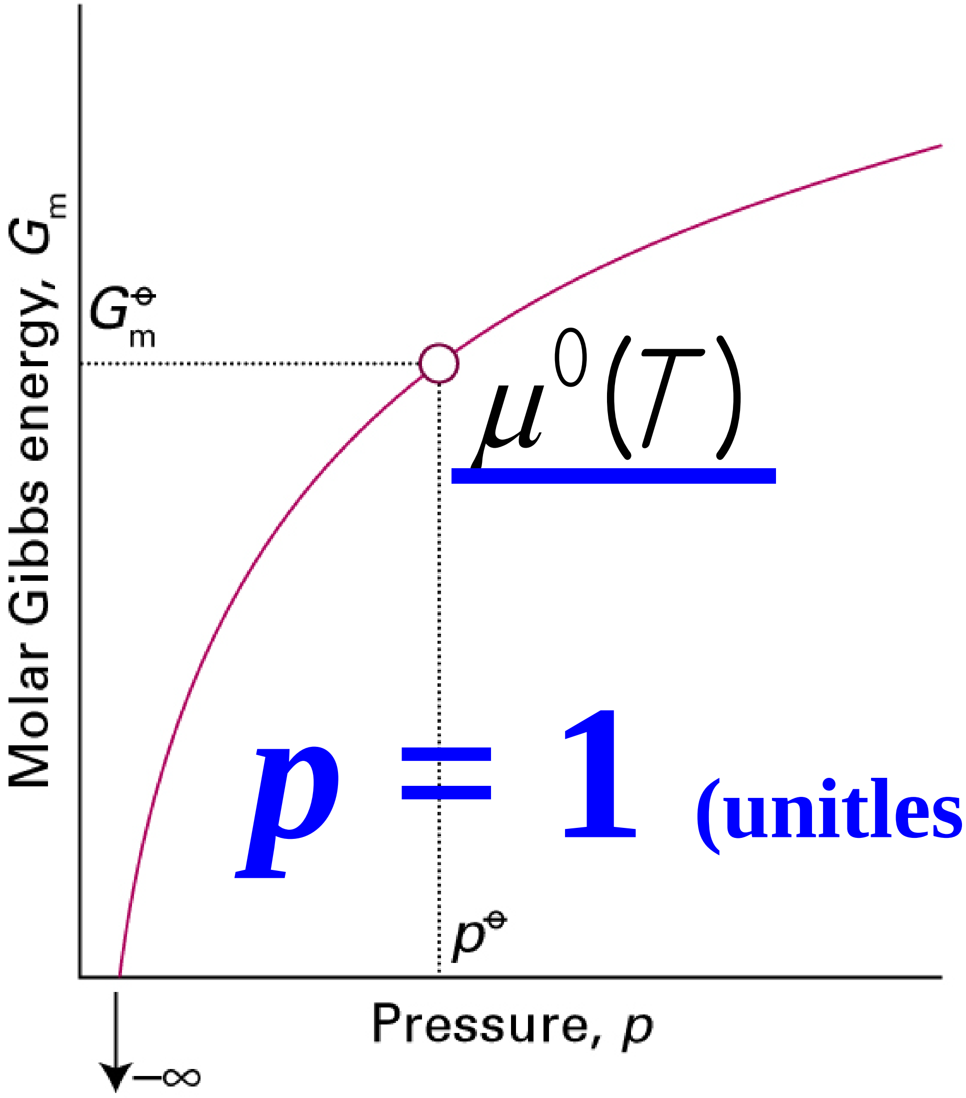
(later)

$$\mu_i(p,T,p_1,p_2,p_3,\ldots) = \mu^0{}_i(p,T) + RT\ln p_i$$

Ideal Gas

Single Component + Ideal Gas

$$\mu(p,T) = G_m(p,T) = \mu^0(T) + RT \ln p$$



$$\underline{\mu^0(T)}$$

$$\boldsymbol{p = 1}$$ **(unitless)**

Figure 3D.6

The molar Gibbs free energy of a perfect gas is proportional to ln *p*.

(skip)

Real Gases: the Fugacity

$G_m(p) = G_m^0 + RT\ln(p/atm)$: applicable to ideal gases

For real gases, we are to determine the pressure dependence of the volume of a sample of real gas and to calculate $G(p)$ from $\int V(p)dp$ by numerical integration.

$$G_m = G_m^0 + RT\ln(f/atm) \Rightarrow \mu = \mu^0 + RT\ln(f/atm)$$

The quantity f plays the role of the pressure, but it has a value which ensures that the chemical potential is given by the last equation whatever the pressure. Here f is called as the fugacity of gas.

The following equation is true for all substances.

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V(p)dp;\ G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m(p)dp$$

Hence, for a real gas,

$$\int_{p_i}^{p_f} V_m^{real}dp = \mu^{real}(p_f,T) - \mu^{real}(p_i,T) = RT\ln\frac{f_f}{f_i}$$

(skip)

For an ideal gas,

$$\int_{p_i}^{p_f} V_m^{real} dp = \mu^{real}(p_f, T) - \mu^{real}(p_i, T) = RT \ln \frac{f_f}{f_i}$$

The difference of the two equations

$$\int_{p_i}^{p_f} \left\{ V_m^{real}(p) - V_m^{ideal}(p) \right\} dp = RT \ln \frac{f_f}{f_i} - RT \ln \ln \frac{p_f}{p_i}$$

$$\ln \left\{ \frac{(f_f / p_f)}{(f_i / p_i)} \right\} = \frac{1}{RT} \int_{p_i}^{p_f} \left\{ V_m^{real}(p) - V_m^{ideal}(p) \right\} dp$$

$$p_i \to 0 \quad \frac{f_i}{p_i} \to 1$$

$$\ln\left(\frac{f}{p} \right) = \frac{1}{RT} \int_0^p \left\{ V_m^{real}(p) - V_m^{ideal}(p) \right\} dp$$

$$V_m^{ideal} = \frac{RT}{p}$$

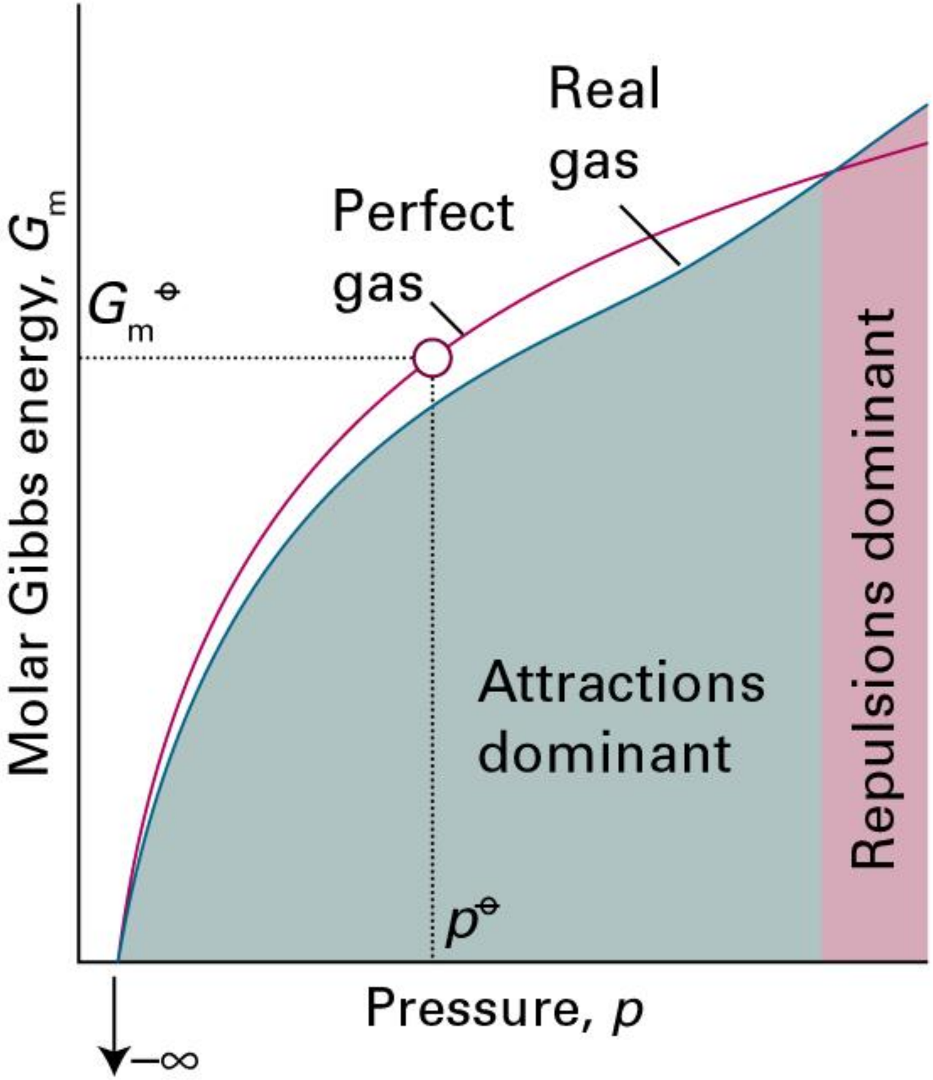


Figure 3.25

The molar Gibbs free energy of a real gas. As $p \to 0$, the molar Gibbs free energy coincides with the value for a perfect gas. When attractive forces are dominant (at intermediate pressures), the molar Gibbs free energy is less than that of a perfect gas and the molecules have a lower 'escaping tendency'. At high pressures, when repulsive forces are dominant, the molar Gibbs free energy of a real gas is greater than that of a perfect gas. Then the 'escaping tendency' is increased.

(skip)

The Real Volume-Pressure Dependence

Compression factor

$$z = \frac{pV_m^{real}}{RT} \Rightarrow V_m^{real} = \frac{zRT}{p}$$

For a real gas, $z = z(p, T)$

$$\ln\left(\frac{f}{p}\right) = \frac{1}{RT}\int_0^p \left\{V_m^{real}(p) - V_m^{ideal}(p)\right\} dp$$

$$\ln\left(\frac{f}{p}\right) = \frac{1}{RT}\int_0^p \left(\frac{zRT}{p} - \frac{RT}{p}\right) dp = \frac{RT}{RT}\int_0^p \left(\frac{z(p,T)-1}{p}\right) dp$$

$$= \int_0^p \frac{z(p,T)-1}{p} dp$$

$$\therefore\ f = p \exp \int_0^p \left(\frac{z(p,T)-1}{p}\right) dp$$

Standard States of Real Gases

For an ideal gas, p = 1*atm*: standard state

For a real gas, f = 1*atm*: standard state

$$f=\gamma p$$

g : fugacity coefficient

$$\mu(p)=\mu^0+RT\ln(f/atm)$$

$$\mu(p)=\mu^0+\underbrace{RT\ln(p/atm)}_{}+\underbrace{RT\ln\gamma}_{}$$

The chemical potential of an ideal gas

Deviation from ideality

(선행 학습)

Open System and Changes of Composition

$$dG = -SdT + Vdp$$

$$G = \sum_i \mu_i n_i$$

At constant pressure and temperature, Gibbs function has no changes. However, when composition change, Gibbs function changes.

$$\therefore G(p,T) \Rightarrow G(p,T,n_1,n_2,n_3,\cdots)$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i$$

where n_1, n_2, … are the amount of substances 1, 2, …present.

Derivation in Chap. 5

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2\cdots} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2\cdots} dT \qquad (1)$$

$$+ \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2,n_3\cdots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1,n_3\cdots} dn_2 + \cdots$$

Let the composition be fixed and permit only the temperature and pressure to change.

$$\left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2\cdots} = V \qquad (2); \qquad \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2\cdots} = -S \qquad (3)$$

Suppose now that substance 1 is the only substance present. **(선행 학습)**

$G \propto$ the amount of material present

$$G = n_1 G_{1m} = n_1 \mu_1$$

At constant temperature and pressure,

$$dG = \mu_1 dn_1$$

$$\left(\frac{\partial G}{\partial n_1}\right)_{p,T} = \mu_1$$

Therefore, the chemical potential of species 1 is the measure of how the Gibbs function of species 1 changes when the amount present is varied.

More than One Component:

$$\mu_i\left(T, p, n_j\right) \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \qquad (4)$$

in Chap. 5

(as a definition)

↓

<u>Partial Molar Gibbs Free Energy</u> for atom *i*

= <u>Chemical Potential</u> for atom *i*

Substituting eqs (2), (3) and (4) into eq (1), one obtains

$$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + \cdots$$

(later)

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_1,n_2\cdots} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2\cdots} dT$$

$$+ \left(\frac{\partial G}{\partial n_1}\right)_{p,T,n_2,n_3\cdots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{p,T,n_1,n_3\cdots} dn_2 + \cdots$$

More general form

$$dG(T, p, n_j) = -SdT + Vdp + \sum_i \mu_i dn_i$$

(reversible)

진짜 물질

the master equation of chemical thermodynamics

Derivation in Chap. 5

Entropy (Boltzmann Formula) + 열역학 제2법칙 짱 중요

Binary alloy에서 μ_A and μ_B 측정 방법: 선행 학습 (Chap. 5)

Problems from Chap. 3

3A.2

3A.1(b) 3A.2(b) 3A.3(b) 3A.5(b) 3A.7(b)

3A.2

3B.8

3D.2

3D.1(b) 3D.2(b) 3D.3(b)

3.2